NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 4032

REDUCTION OF OXIDIZED NICHROME V POWDERS AND SINTERING OF NICHROME V BODIES

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SUMMARY

This investigation was conducted to determine the effectiveness of the deoxidation and sintering techniques by comparing the strengths and microstructures of powder-metallurgy specimens with those of wrought specimens, to determine the effect of residual-oxide content on the tensile properties of powder-metallurgy specimens, and to evaluate different methods of obtaining essentially oxide-free powders by these determinations.

The three methods used to reduce three lots of oxidized Nichrome V alloy powder at a temperature range of 1800° to 2150° F consisted of (1) tumbling the powder in contact with hydrogen in a rotary tube furnace, (2) heating the oxidized powder in contact with sodium hydride in a hydrogen atmosphere, and (3) heating the oxidized powder in contact with carbon in a hydrogen atmosphere. All three reduction methods were, in most cases, reasonably effective in lowering the oxygen content of as-received powder. The reduction technique utilizing hydrogen and a rotary-tube furnace gave slightly better results, as measured by oxygen analyses, than the other reduction methods and was, by far, the most convenient to use.

Several powder specimens had mechanical properties and microstructures essentially equivalent to those of the wrought specimens. In general, no correlation existed between the tensile properties of specimens and oxide content. However, in cases where the oxygen content was extremely high, the density was low. This low density was probably responsible for the low tensile values recorded for these specimens.

INTRODUCTION

Fabrication of products by powder-metallurgy techniques is of increasing interest in the field of flight propulsion. In this field a critical need exists for materials able to withstand large stresses at high temperatures. As a result, refractory materials such as molybdenum, niobium, certain oxides and borides, and combinations of ceramics and metals (cermets), all of which are of potential use at extremely high temperatures, are being investigated. Because of the refractory nature of many of these materials, powder metallurgy offers the most practical method of fabrication (although metals, such as molybdenum and niobium, have been successfully arc-melted and cast). This method also provides well-known advantages such as low machining and finishing costs as well as a method for fabricating parts requiring controlled porosity.

In the fabrication of high-temperature components, perhaps the most serious disadvantage of powder metallurgy is uncontrolled porosity in the finished product. Powder-metallurgy parts generally have strengths lower than their cast or forged counterparts, and these low strength values have been attributed to porosity (ref. 1). For many room-temperature applications, lower strengths can be tolerated, and fabrication by the powder-metallurgy process would be economical. On the other hand, for many high-temperature applications (such as uncooled turbine buckets), high strengths are essential, and uncontrolled voids therefore must be eliminated. Successful elimination of voids and the obtaining of strengths equivalent to, or better than, those of cast materials have been achieved in certain cases by the use of hot coining following sintering (ref. 2).

Perhaps the greatest advantage of the powder-metallurgy process, compared with the more conventional methods of fabrication, is its use as a research tool to study the fundamental properties of alloys. An interesting discussion of the uses is given in reference 3. Powder metallurgy permits great latitude in structural and compositional control. For example, in conventionally cast and forged materials, the structure may be altered to some degree by controlling alloying elements and pouring temperature, by heat treatment, by hot and cold work (and the like). In addition to most of these ways of varying structure, powder metallurgy offers a means (unavailable in conventional methods of alloy production) of varying the composition, shape, quantity, and distribution of microconstituents in alloys. Also, many types of nonequilibrium structures that normally would not appear in a cast or forged alloy may be obtained when the same alloy is fabricated by powder-metallurgy procedures. By utilizing powder-metallurgy techniques to vary structure, it may be possible to improve the physical properties of many heat-resistant alloys. Most heat-resistant alloys are extremely complex and their structures contain a variety of such compounds as carbides and intermetallics as dispersions, networks, or combinations of the two. As in other alloys, the microstructural configuration of heat-resistant alloys is known to effect creep resistance and stress-rupture strength (ref. 4), but the specific effects of different microconstituents and their configurations are not known.

Because of its potential value as a research tool, a preliminary powder-metallurgy program has been initiated at the NACA Lewis laboratory. The over-all program was designed to study the effects of variations in quantity and distribution of microconstituents on the strength properties of various heat-resistant alloys produced by powder-metallurgy methods. The present report covers a preliminary phase of work on the standardization of techniques for producing essentially oxide-free powders and for fabricating components from them. This work was considered necessary since, in subsequent work involving the controlled additions of microconstituents, uncontrolled oxide inclusions would lead to questionable results.

The main objectives were the determination of the effectiveness of the deoxidation and sintering techniques by comparing the strengths and microstructures of powder-metallurgy specimens with those of wrought specimens, the determination of the effect of residual-oxide content on the tensile properties of powder-metallurgy specimens, and the evaluation of different methods of obtaining essentially oxide-free powders by these determinations.

Oxidized Nichrome V alloy powder from three sources was deoxidized by three different reduction methods. The deoxidized powders were hydrostatically pressed, sintered, and hot-swaged into rod. Evaluation of the deoxidation methods was made by means of room-temperature tensile tests, oxygen analyses, microstructures, and densities of the swaged rod.

MATERIALS, APPARATUS, AND PROCEDURE

Materials

Nichrome V alloy (80 percent Ni - 20 percent Cr) was selected for this investigation because:

(1) It is the base for a large group of high-temperature alloys.

(2) It is a single-phase alloy having no precipitation-hardening or other phenomena to complicate the interpretation of physical tests on specimens made from this powder.

(3) The oxide found on the surface of this alloy is mainly chromic oxide Cr_2O_3 or nickel monoxide and chromic oxide $NiO \cdot Cr_2O_3$ (ref. 5), both of which are adequate for tests of reduction techniques.

Two lots of prealloyed Nichrome V powder were obtained from commercial sources designated A and B. One additional lot was produced at the NACA Lewis laboratory, designated source C. A range of particle sizes was obtained, but only -100 mesh particles were used in the present investigation. The typical particle-size distribution of powders used in fabricating specimens for this report was as follows:

Mesh size	Percent
-100 to +150	16.1
-150 to +200	16.4
-200 to +270	18.3
-270 to +325	11.0
-325	38.2

Commercial source A produced the powder by disintegrating a molten stream of the metal alloy with a high-pressure water spray. Powder from source B was produced by the hydride process, in which the powdered alloys are made directly from the corresponding oxides (ref. 6, p. 154). Powder for lot C was produced by passing 3/16-inch Nichrome V alloy rods through a commercial metallizing gun that burns a mixture of acetylene and oxygen. Molten metal was sprayed from the nozzle of the gun into a flowing water bath as shown in figure 1.

A film of oxide was visible on the surface of all powders. The cleanest powder appeared to be that obtained from source B, while source C powder was the most heavily oxidized.

Apparatus and Procedure

Three reduction techniques were used to remove the oxide film from the powder; the reducing agents were

(1) Purified hydrogen

(2) 1-Percent sodium hydride plus purified hydrogen

(3) 1-Percent carbon plus purified hydrogen

The hydrogen was purified by passing through a palladium catalyst furnace at about 300° F, an activated-alumina drying tower, and a liquid-nitrogen cold trap (fig. 2). The purified gas had a dewpoint of less than -100° F.

In the first method, the powder was tumbled in a rotary furnace (fig. 2) while purified hydrogen was passed through the furnace. In the other methods, the powder plus either sodium hydride or carbon additions was placed in a tray in a sand-sealed box, and purified hydrogen was passed through the box. In all techniques the reduction temperature was between 1800° and 2150° F, and reduction was considered complete when the powder showed a bright metallic luster.

After cleaning, the powder was mixed with a solution of 0.5-weight-percent paraffin in benzene. Trial compacts using both 1.0-weight-percent paraffin and no paraffin were also made; but compacts with no paraffin had insufficient green strength, while compacts with 1.0-percent paraffin had lower densities after sintering than were desirable. The benzene was subsequently evaporated, leaving the powder particles coated with a thin film of paraffin binder.

All compacts used in this investigation were hydrostatically pressed. The powders were sealed in 4-inch lengths of 5/8-inch-diameter rubber tubing, placed in an oil-filled die chamber, and pressed to 25 tons per square inch with no dwelling time at pressure.

The green compacts were then sintered in vacuum (1 to 2 microns) in a tungsten-wound resistance furnace. Various sintering times and temperatures were investigated; the most satisfactory combination of times and temperatures, determined from density measurements (a density greater than 90 percent of theoretical density after sintering was considered satisfactory), was 6 hours at 2400° F. All data reported in this investigation were obtained from specimens sintered under these conditions.

After sintering, the specimens were sealed in evacuated Inconel tubes and hot-swaged at 2150° F. The apparent reduction in area was about 75 percent, but part of this value represents the closing of voids and the densification of the compact. The true reduction in area was probably about 60 to 65 percent.

Following swaging, the Inconel tubes were mechanically removed and tensile specimens were machined from the swaged bars; diameters of test specimens ranged from 0.161 to 0.205 inch, with a gage length of approximately 2 inches. After machining, the specimens were stress-relief annealed in vacuum for 2 hours at 1200° F.

Twenty tensile specimens, representing the three lots of powder and the three reduction methods, were tested at room temperature (table I). Wrought bar stock also was tested as a basis for comparison.

In addition to tensile tests, densities were measured by the water-displacement method, and the specimens were examined metallographically for oxide inclusions and voids.

The quantitative analysis of oxide content was performed at commercial laboratories by vacuum fusion and bromination techniques.

RESULTS AND DISCUSSION

Evaluation of Deoxidation Methods by Tensile Tests

Room-temperature tensile properties of specimens are tabulated in table I. Tensile strength of powder-metallurgy specimens ranged from 83,700 to 119,600 pounds per square inch. The specimens fabricated from powders produced by the hydride process (source B) generally had greater tensile strengths than specimens fabricated from powders atomized by a water spray (source A) or from powders made with a metallizing gun (source C). 4342

The methods of deoxidizing powders seemed to be capable of equal effectiveness. For example, the properties of specimens made from powders deoxidized by

(a) Hydrogen in a retort - specimens 2, 7, and 8

(b) Sodium hydride plus hydrogen - specimens 9 and 10

(c) Carbon plus hydrogen - specimens 11 and 18

had nearly equivalent strengths and ductilities. The strengths ranged from 103,900 to 119,600 pounds per square inch, and the ductilities, as measured by reduction in area, ranged from 38 to 52 percent. For the groups having the best strength (source B powder), the hydrogen-reduced specimens and the hydrogen-plus-sodium-hydride - reduced specimens had strengths that were approximately equivalent.

Specimens made from source C powder deoxidized with sodium hydride plus hydrogen (specimens 15, 16, and 17) had low tensile strengths of 84,300, 84,600, and 83,700 pounds per square inch, respectively. The low tensile strengths of these specimens may be attributed to their low densities, which were about 94 percent of theoretical density (table I).

Although none of the specimens made by the powder-metallurgy method had strengths fully equivalent to the strength of the wrought material (125,200 and 126,200 psi - specimens 19 and 20), several specimens had strengths that approach these values. For example, specimens 8, 9, and 10 had strengths ranging from 117,200 to 119,600 pounds per square inch.

Evaluation of Deoxidation Methods by Oxygen Analysis

The results of the oxygen analyses by the vacuum fusion and the bromination methods are presented in table II. It may be observed that the vacuum-fusion results had some scatter; for example, three separate analyses of specimen 20, which had been machined from a piece of wrought bar stock, yielded oxygen contents ranging from 0.0044 to 0.054 percent. 4342 Such a scatter seems unrealistic for a wrought bar that presumably should be chemically homogeneous. Since two of the specimen-20 analyses agree reasonably well while the third analysis is higher by a factor of about ten, the high value is considered erroneous and therefore is discarded. The single bromination-method analysis of the wrought material (0.034 percent) was higher than the values obtained by the vacuum fusion method (with the exception of the one discarded value). Since metal chips are analyzed in the bromination method, the analyzed oxygen content of the chips could be higher than the actual oxygen content of the bulk material because of possible oxidation of the metal chips during machining.

In the cases of specimens 3, 11, and 15, abnormally high oxygen contents might have resulted partly from leaks that may have occurred in the welded portion of the Inconel sheaths used in the hot-swaging of the specimens. With these exceptions, it appears that the oxygen contents of the powder-metallurgy specimens were generally less (and sometimes appreciably less) than the oxygen contents of the original powders. This trend is evident in both the bromination and vacuum-fusion results. The oxygen analyses also indicate that, for each powder type used (whether the powder was produced by atomization with a water spray, by the hydride process, or by atomization in a metallizing gun), the deoxidation of the powders by hydrogen in a tube furnace was generally more complete than the deoxidation by other methods investigated.

Evaluation of Deoxidation Methods by Density Measurements

Specimen density and percentage of theoretical density are tabulated in table I. The densities of all powder-metallurgy specimens are at least 98 percent of theoretical density with the exception of specimens 15, 16, and 17. The low density (94 percent of theoretical density) of these specimens may have been caused largely by high oxygen content (e.g., 0.99 percent, as measured in specimen 15 of this lot, (table II)).

Evaluation of Deoxidation Methods by Metallographic Examination

Typical microstructure of wrought Nichrome V alloy and powder-metallurgy specimens of this alloy are shown in figures 3 to 6. In figures 4(a) and 5(a) (unreduced source A and B powders), the photomicrographs show specimens made from unreduced powders that had been pressed, sintered, and swaged. It was not possible to sinter (at 2400° F for 6 hr) unreduced powders from source C, and therefore no photomicrograph of this powder in the unreduced condition could be taken. The inability to sinter this material is an indication of its very high oxygen content (0.49 percent).

Comparison of the photomicrograph of the wrought material (fig. 3) with other photomicrographs (e.g., figs. 4(b), (c), and (d), figs. 5(b) and (c), and fig. 6(c)) shows that several specimens had microstructures comparable to that of the wrought material.

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For source A and B powders (figs. 4 and 5), the deoxidation treatments appeared effective in reducing the oxide content of the as-received powders; for example, the specimens made from deoxidized powders of each source (fig. 4(b), (c), and (d) and figs. 5(b), (c), and (d)) had fewer oxides than specimens made from unreduced powders (figs. 4(a) and 5(a)).

Metallographic examinations indicate that powder made by atomization with a water spray (fig. 4, source A) could be more thoroughly deoxidized than powders produced by other methods (figs. 5 and 6, sources B and C), regardless of the type of deoxidation treatment. This result is logical since atomized powder has only a thin film of surface oxide (fig. 4(a), while powder made by the hydride process (oxide reduction) has large internal oxides (fig. 5(a)). (Surface-oxide reduction requires only a surface reaction, while reduction of internal oxides involves a slower diffusion process.) Although deoxidation was arbitrarily considered complete when the powder showed a bright metallic luster, nevertheless powder made by the hydride process could have a bright metallic surface after deoxidation treatment but still contain many internal oxides. On the other hand, when atomized powder showed a bright metallic luster, most of its oxides (surface oxides) had been reduced.

Powder produced in the metallizing gun (source C) contained surface oxides similar to those on atomized powder, but to a greater extent; this powder therefore was much more difficult to deoxidize as completely as atomized powder.

Although the specimens made from source B powder (fig. 5) appeared to have more oxide inclusions after deoxidation than other specimens, they nevertheless had the greatest tensile strengths, as pointed out previously. This observation suggests that internal or globular oxides are generally less harmful than oxides that form on the surface of the powder and appear as grain-boundary oxides when this powder is pressed and sintered.

SUMMARY OF RESULTS

This investigation was conducted to evaluate three methods of obtaining essentially oxide-free Nichrome V alloy powder. Evaluation was made by means of oxygen analyses, tensile tests, and microstructure of specimens made from deoxidized powders. The results show that:

1. The reduction methods investigated were, in most cases, reasonably effective in lowering the oxide content of as-received powder.

2. The reduction technique utilizing hydrogen and a rotating-tube furnace gave slightly better results, as measured by oxygen analyses, than the other reduction methods and was, by far, the most convenient to use.

3. Several powder specimens had mechanical properties and microstructures essentially equivalent to those of the wrought test bars.

4. No consistent relationship existed between the tensile properties of specimens and their oxide content, as revealed by oxygen analyses and metallographic studies. However, specimens having extremely high oxygen contents and low densities had correspondingly low tensile strengths.

5. From the standpoint of microstructural studies, the group of specimens appearing to have the greatest number of oxide inclusions had the best tensile strengths. These inclusions were globular in form and randomly dispersed throughout the structure.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, June 3, 1957

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TABLE I. - DENSITY AND ROOM-TEMPERATURE TENSILE PROPERTIES

Source	Specimen number	Method of reduction	Ultimate strength, psi	Reduction in area, percent	Density, g/cm^3	Theoretical density, percent
A	1	H_2	Bent on loading			
	2	H_2	103,900	46	8.42	100.2
	3	H_2 + NaH	92,500	47	8.40	100.0
	4	H_2 + NaH	93,000	43	8.40	100.0
	5	H_2 + C	92,100	59	8.48	100.9
	6	H_2 + C	90,900	57	8.48	100.9
B	7	H_2	111,500	52	8.38	99.7
	8	H_2	118,600	45	8.38	99.7
	9	H_2 + NaH	119,600	42	8.35	99.4
	10	H_2 + NaH	117,200	40	8.36	99.6
	11	H_2 + C	104,600	38	8.24	98.1
	12	H_2 + C	104,500	22	8.30	98.8
C	13	H_2	96,400	32	8.27	98.4
	14	H_2	90,000	30	8.27	98.4
	15	H_2 + NaH	84,300	25	7.93	94.4
	16	H_2 + NaH	84,600	23	7.94	94.5
	17	H_2 + NaH	83,700	--	7.93	94.4
	18	H_2 + C	114,000	43	8.34	99.3
Wrought	19		125,200	57	----	----
	20		126,200	55	----	----

TABLE II. - OXYGEN ANALYSES

Source	Specimen number	Method of reduction	Oxygen by weight, percent	Method of oxygen determination
A		No reduction; as-received powder	0.24	Bromination
B		No reduction; as-received powder	.385	Vacuum fusion
B		No reduction; as-received powder	.167	Vacuum fusion
B		No reduction; as-received powder	.22	Bromination
C		No reduction; as-received powder	.49	Bromination
A	1	H_2	0.063	Bromination
	2	H_2	.033	Vacuum fusion
	3	H_2 + NaH	.347	Vacuum fusion
	4	H_2 + NaH	-----	-------------
	5	H_2 + C	.060	Vacuum fusion
	6	H_2 + C	-----	-------------
B	7	H_2	0.11	Bromination
	8	H_2	.057	Vacuum fusion
	9	H_2 + NaH	.125	Bromination
	10	H_2 + NaH	.090	Vacuum fusion
	11	H_2 + C	.50	Vacuum fusion
	12	H_2 + C	.278	Vacuum fusion
C	13	H_2	0.103	Bromination
	14	H_2	.197	Vacuum fusion
	15	H_2 + NaH	.99	Vacuum fusion
	16	H_2 + NaH	-----	-------------
	17	H_2 + NaH	-----	-------------
	18	H_2 + C	.270	Vacuum fusion
Solid wrought rod	19		0.034	Bromination
	20		.0078	Vacuum fusion (analysis 1)
			.0044	Vacuum fusion (analysis 2)
			.054	Vacuum fusion (analysis 3)

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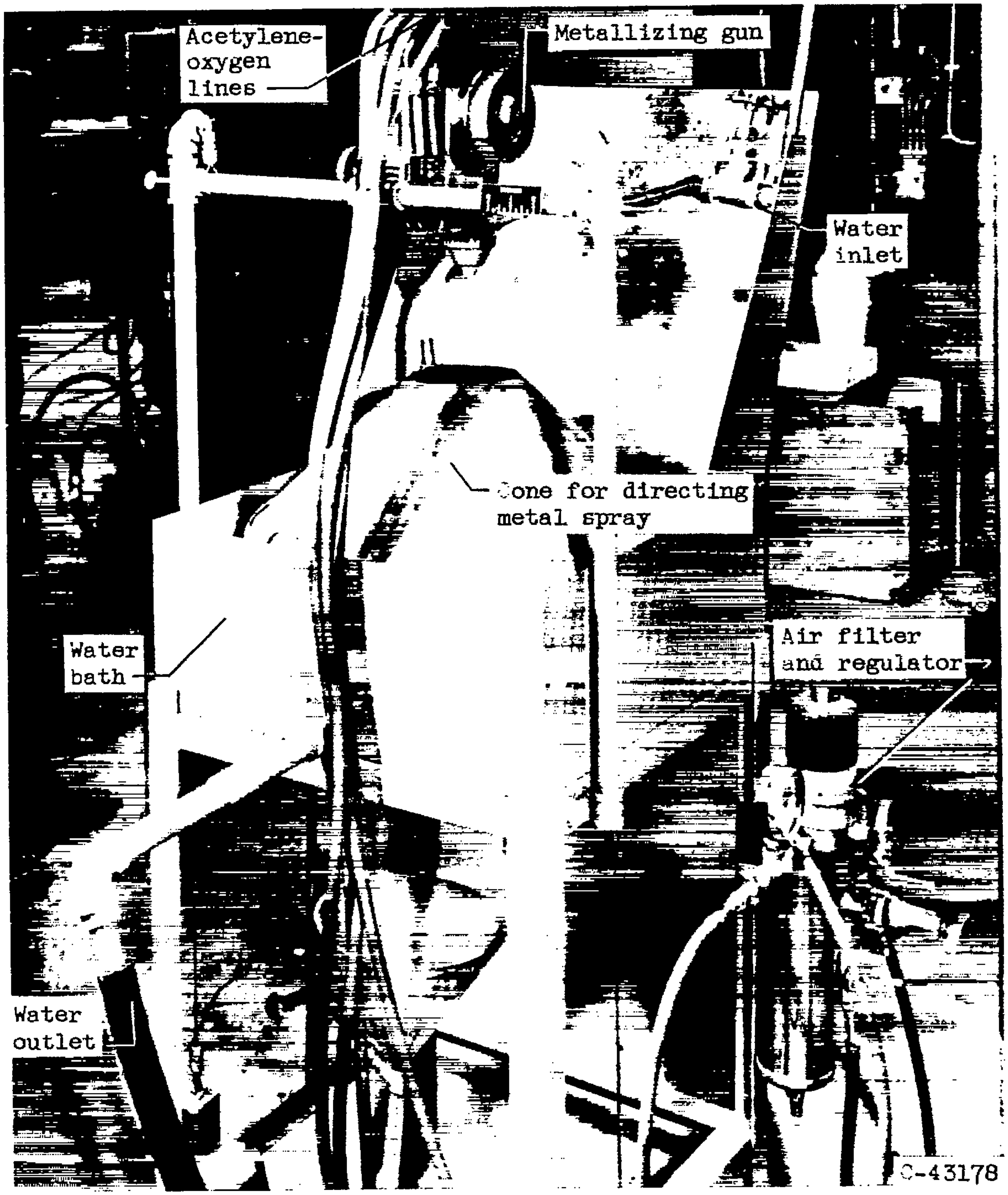

Figure 1. - Powder spraying apparatus.

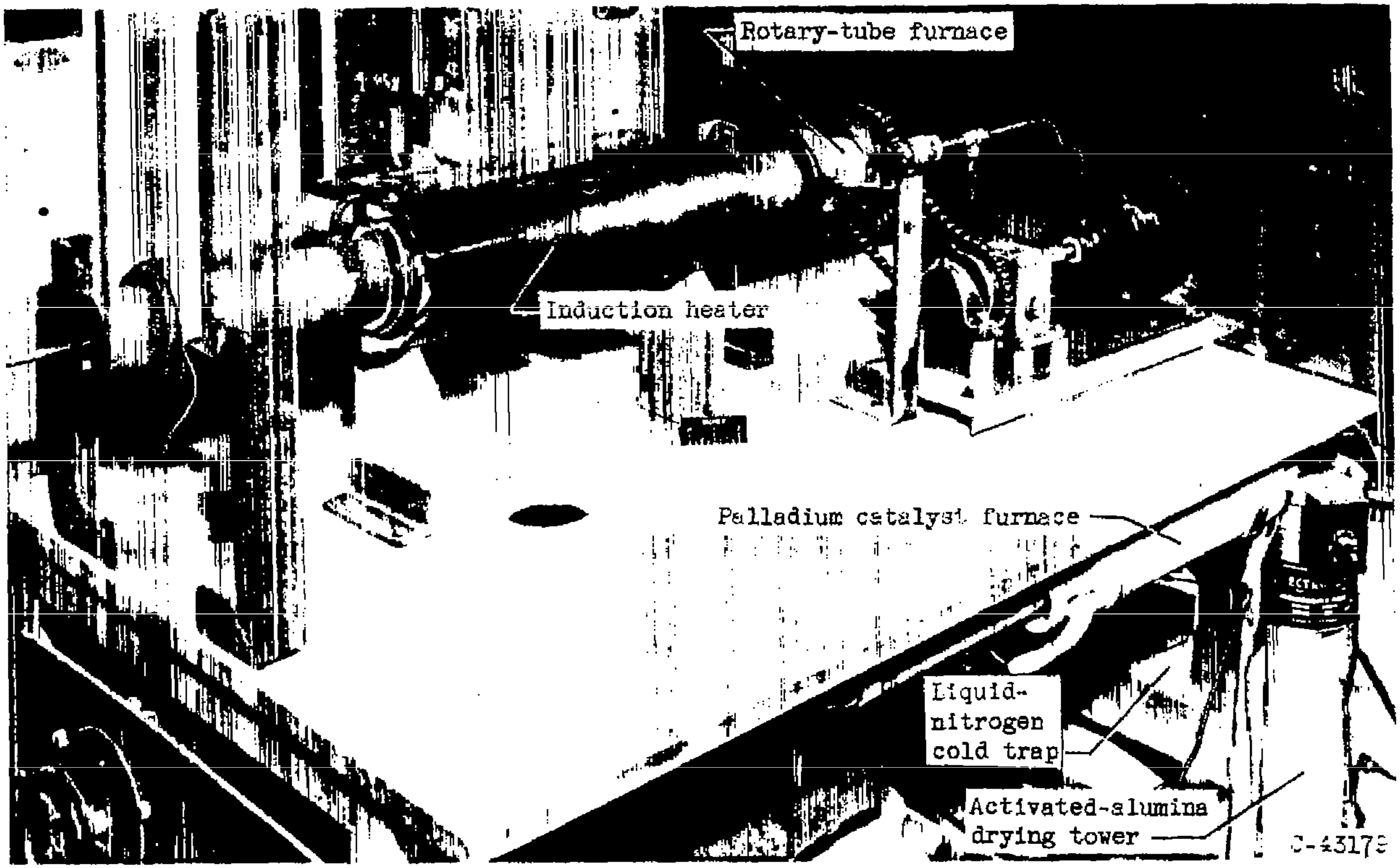

Figure 2. - Rotating-tube reduction furnace.

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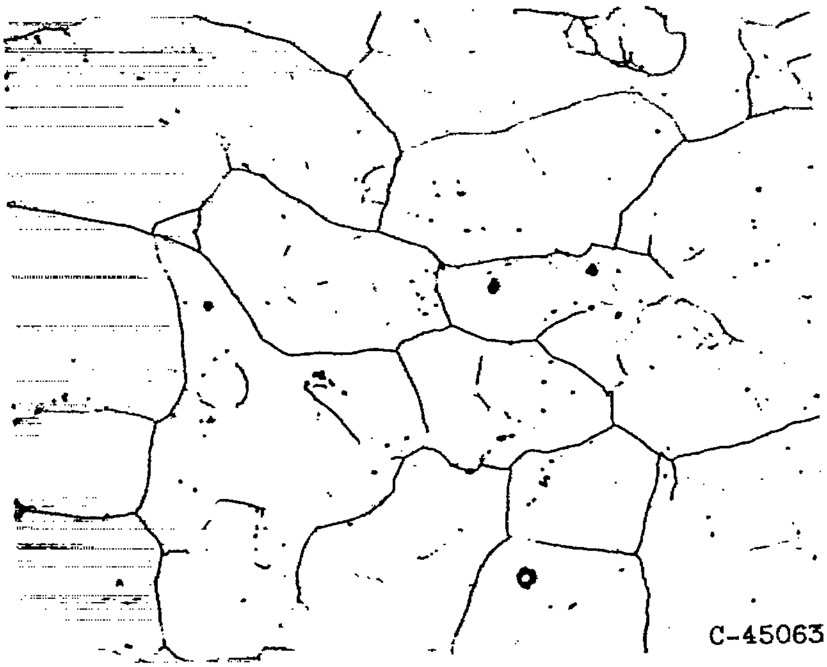
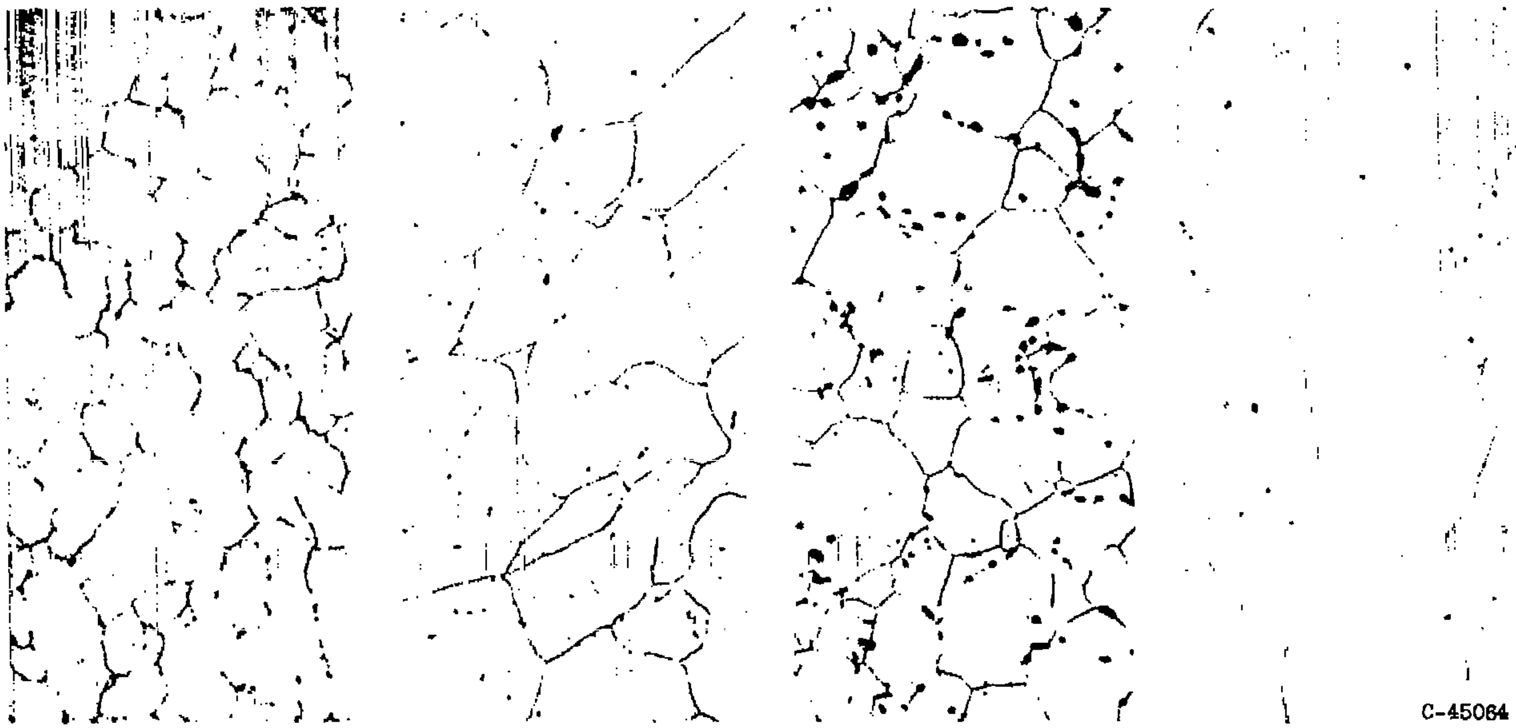
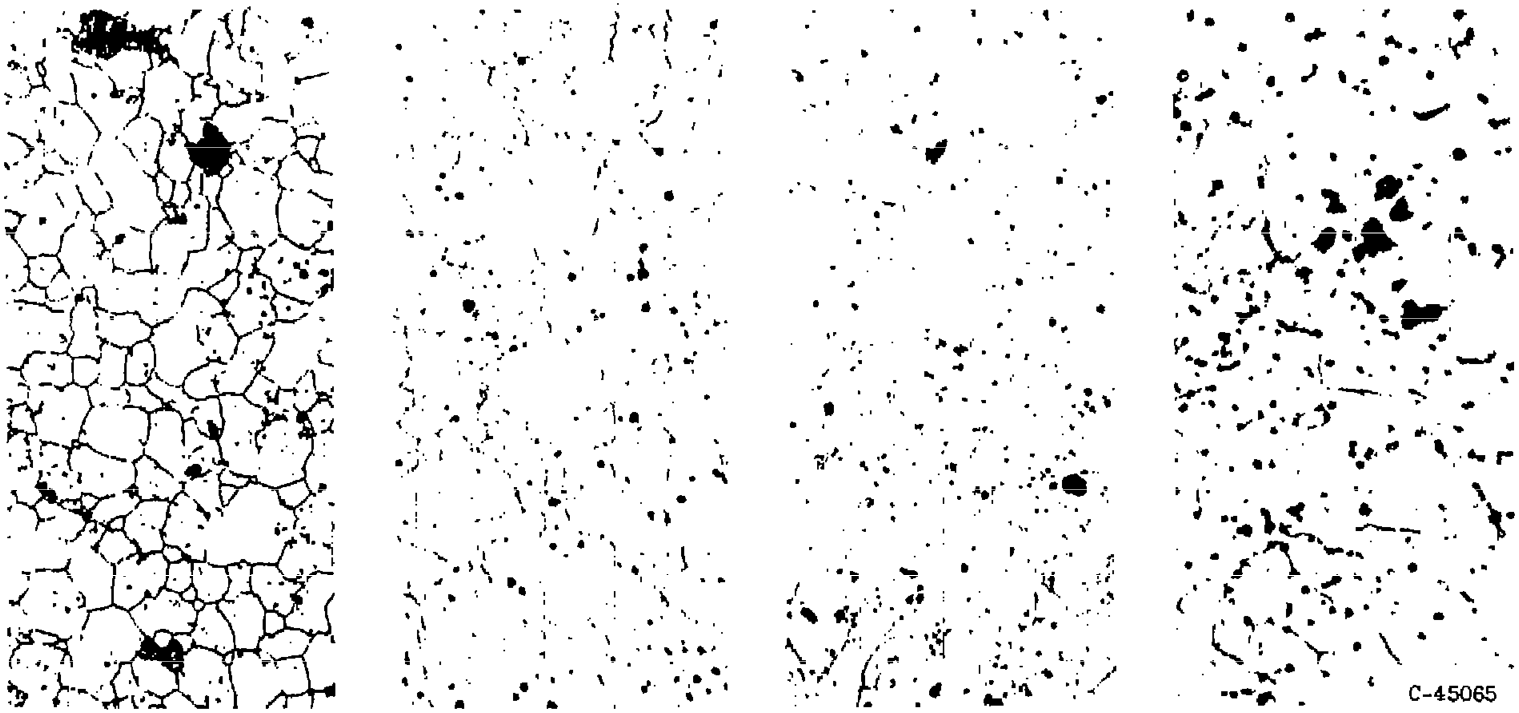


Figure 3. - Wrought Nichrome V rod, hot-swaged. Etchant, Carapella's Reagent; X500.



(a) As received. (b) Deoxidized with H_2. (c) Deoxidized with NaH plus H_2. (d) Deoxidized with C plus H_2.

Figure 4. - Powder-metallurgy specimens of Nichrome V alloy. Powder was produced by atomization of molten alloy by water spray (source A). Specimens were made from powder in as-received and deoxidized conditions by pressing, sintering, and hot-swaging. Etchant, Carapella's Reagent; X500.



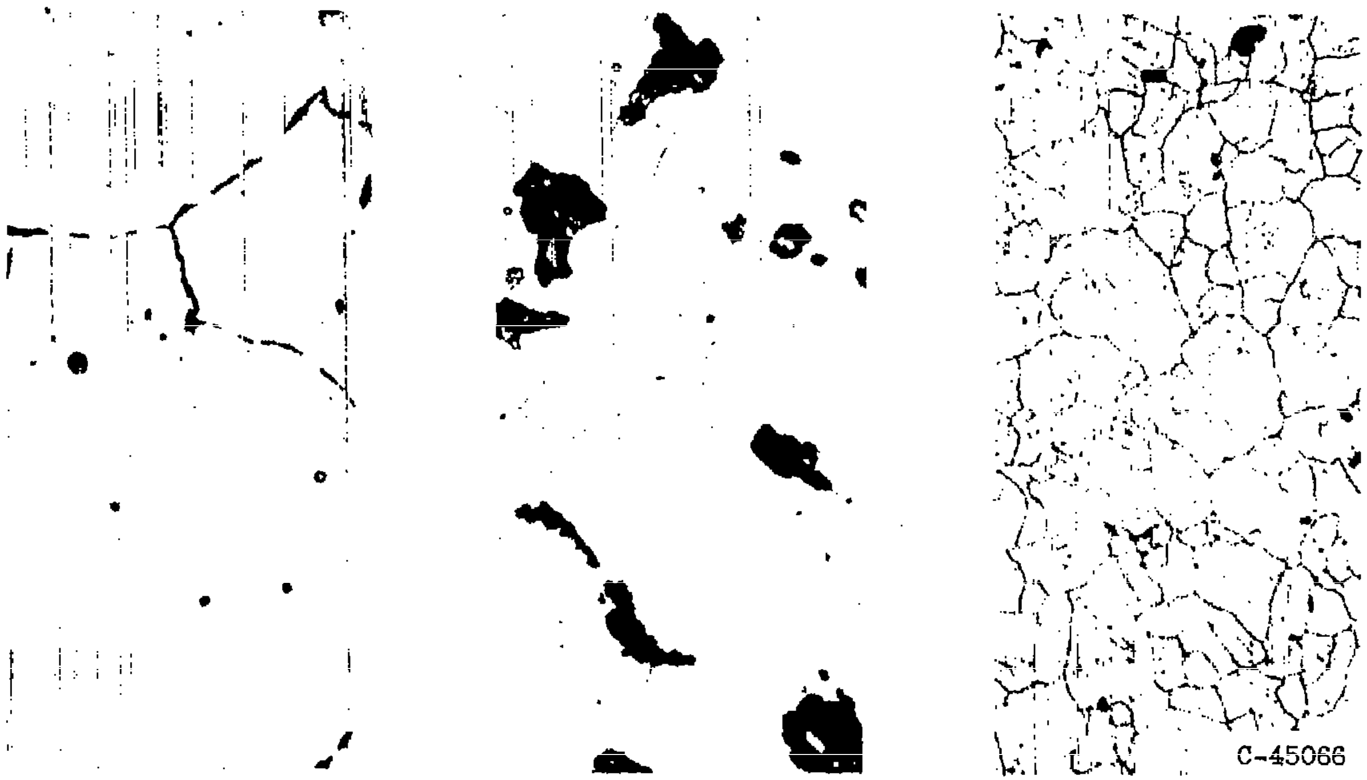
(a) As received.

(b) Deoxidized with H_2.

(c) Deoxidized with NaH plus H_2.

(d) Deoxidized with C plus H_2.

Figure 5. - Powder-metallurgy specimens of Nichrome V alloy. Powder was produced by hydride process (source B). Specimens were made from powder in as-received and deoxidized conditions by pressing, sintering, and hot-swaging. Etchant, Carapella's Reagent; X500.



(a) Deoxidized with H_2.

(b) Deoxidized with NaH plus H_2.

(c) Deoxidized with C plus H_2.

Figure 6. - Powder-metallurgy specimens of Nichrome V alloy. Powder was produced by atomization of alloy rod with metallizing gun (source C). Specimens were made from powders in deoxidized condition by pressing, sintering, and hot-swaging. Etchant, Carapella's Reagent; X500.